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At ARS, the Atmosphere Is Right for Air Emissions Studies

At a study site in Beltsville, Maryland, ARS researchers measure agricultural herbicides that volatilize into the air after they are applied to the field. Soil scientist Lynn McKee (foreground) works on the pesticide air sampler while micrometeorologist John Prueger (left) adjusts the controls on the manifold and soil scientist Tim Gish downloads micrometeorological data. **(D2241-1)**

"Air doesn't have any boundaries," says Agricultural Research Service (ARS) chemist Laura McConnell. "So when we study the dynamics of different components that affect air quality, we're trying to figure it out in an open system. For instance, maybe the compound we're studying comes from a local source—or maybe it's coming from a hundred miles away."

"This kind of research is a real challenge," agrees Charlie Walthall, who is the national program leader for ARS's work on air emissions. "But there is a substantial payoff for farmers and for the public. We are working to develop management practices that increase the efficiency of agricultural production and that also protect and enhance our soil, water, and air."

As part of this effort, McConnell is just one of dozens of ARS scientists conducting research in a system where controls are hard to come by. She has teamed up with ARS chemist Cathleen Hapeman, who works with McConnell at the ARS Environmental Management and Byproducts Utilization Laboratory in Beltsville, Maryland, to identify factors that affect pesticide levels in the Chesapeake Bay region "airshed." Some of these pesticides, including organochlorine insecticides and their breakdown products, are considered "legacy" pesticides because, even though farmers are no longer permitted to use them, trace levels of the chemicals can still be detected in the air, soil, and water.

Tracking Trace Chemicals

Working with partners at the University of Maryland and the University of Delaware, the scientists established three monitoring stations in the Chesapeake Bay Watershed. One was near the Choptank River in Cambridge, Maryland. A second site was located at the University of Delaware in Lewes, and the third was set up at the Delaware National Estuarine Research Reserve in Dover.

Chemists Cathleen Hapeman (left) and Laura McConnell use air and rain sample collection devices to study the fate of atmospheric pollutants in the Chesapeake Bay region. **(D1877-1)**

From 2000 to 2003, the team obtained weekly air samples and rain samples for each precipitation event from the three sites. Then they tested the samples in the lab for several types of legacy pesticides, including chlordane and related chemical products such as heptachlor and breakdown products of chlordane; lindane; aldrin and dieldrin; DDT and its degradation products (DDD and DDE); and mirex.

All of the pesticides were detected in at least one air sample, but they were rarely detected on particles captured from the air. Nearly all the air samples contained lindane and chlordane products, and the pesticides with the highest mean concentrations were dieldrin and DDE.

Cody Howard, an ARS environmental engineer, uses the pesticide emissions model to study and predict agricultural emissions and their effect on air quality in the Chesapeake Bay region.

Here, There, and Everywhere

Results also indicated that some of the legacy pesticides detected in the samples—chlordane compounds, lindane, DDE, and dieldrin—came from local and regional sources, possibly from contaminated soils. When disturbed, the generally sandy soils on the Delmarva Peninsula are more likely to release pesticides than soils with a higher organic carbon content.

But these studies also suggested that most of the lindane, heptachlor, and many of the chlordanes detected in the air samples came from sources more than 60 miles away.

Using models, McConnell and Hapeman also found that variability in air temperature and wind conditions accounted for 30 to 60 percent of the variability of compound levels. And—some good news—with the exception of dieldrin, the half-life values measured for the pesticides in the samples indicated

(D2239-1)

that legacy pesticide levels were decreasing over time in the Delmarva.

"The Chesapeake Bay region is a mix of urban areas and agricultural areas," says Hapeman. "But water quality in the bay itself is highly influenced by atmospheric chemistry, not just by runoff from urban lands and farm lands. These measurement studies and new modeling efforts with ARS environmental engineer Cody Howard are helping us understand the role that past and present agricultural practices and air quality play in restoring and maintaining water quality in the bay."

A Pesticide's Surprising Path

A few fields away in Beltsville, ARS soil scientist Timothy Gish and his colleagues are tackling another piece of the air quality quandary—measuring the amounts of pesticides that evaporate into the air after they're applied to the field. ARS micrometeorologist John Prueger, who works at the National Laboratory for Agriculture and the Environment (NLAE) in Ames, Iowa, is co-leading the investigation with Gish. Other ARS scientists on the study include agronomist Craig Daughtry, hydrologist William Kustas, soil scientist Lynn McKee, and physical scientists Andrew Russ and Joseph Alfieri, who all work with Gish at the ARS Hydrology and Remote Sensing Laboratory. NLAE director Jerry Hatfield is also a project collaborator.

In Beltsville, Maryland, soil scientist Lynn McKee and physical scientist Joseph Alfieri check the surface and subsurface soil moisture monitoring systems at the Optimizing Production Inputs for Economic and Environmental Enhancement (OPE3) study area.
(D2240-1)

The scientists looked at the field dynamics of atrazine and metolachlor, two herbicides commonly used in corn production. Both herbicides are known to contaminate surface and ground water, usually through field runoff. Many experts believed the chemicals had a low volatilization rate—that is, after they were applied to the field, they would not readily evaporate into the atmosphere—and that volatilization was not a contributing factor in local water contamination.

"A lot of research indicated that atrazine and metolachlor runoff increases during or after heavy precipitation," says Gish. "But there had never been a side-by-side comparison of pesticide lost from runoff and volatilization."

So the team set up a 10-year study at the Optimizing Production Inputs for Economic and Environmental Enhancement (OPE3) study area in Beltsville, which was established in 1998 to study major environmental and economic issues facing U.S. agriculture. It is equipped with remote-sensing gear and other instrumentation for monitoring local meteorology, soil, plants, and ground water. This allowed the team to carry out its studies on a well-characterized site where only the meteorology—and the soil water content—would vary.

"We studied the same fields with the same soil types, the same crops, the same management practice, and the same herbicide formulations" Gish says. "But we ended up with different volatilization losses from year to year."

Soil scientist Lynn McKee filters soil samples for pesticide analysis while technician Alex White uses a rotary evaporator to process pesticide samples.
(D2242-1)

Vanishing Into Thin Air

The team observed that when air temperatures increased, soil moisture levels had a tremendous impact on how readily atrazine and metolachlor volatilized into the air—a key factor that had not been included in previous models of pesticide volatilization. When soils were dry and air temperatures increased, there was no increase in herbicide volatilization, but volatilization increased significantly when temperatures rose and soils were wet. Most of the volatilization from wet soils occurred within the first 3 days after the herbicide was applied.

The link between soil moisture and volatilization was highlighted in 2003, when it rained at least once every week in May and June, which prevented the team from planting their experimental corn crops until July. Once the corn was in, it rained again for another 2 weeks. When the skies finally cleared, the scientists were able to apply the herbicides to the soggy fields.

"By this time, the soils were very wet. Five days after we applied the herbicides, we'd lost up to 63 percent of the metolachlor and 12 percent of the atrazine through volatilization," Gish says. "Losses were 35 to 40 percent higher in the wetter spots in the field. Generally, 4 to 5 percent losses are a big deal, so we saw a lot of compounds going off into the atmosphere."

The scientists also noted a correlation between subsoil water movement and herbicide volatilization, a dynamic they could track and document because of the extensive instrumentation at the OPE3 site. As the water rose up through the soil layers and came closer to the surface, volatilization of atrazine and metolachlor increased.

"Sometimes we've also seen volatilization occur when we haven't expected it," Prueger adds. "For instance, we've found that when the soil is dry, volatilization can increase at night because dew formation increases surface soil moisture."

Gish and colleagues plan to take their results and begin looking in more detail at volatilization processes. "Do we have the right set of data to predict pesticide loss? What creates a threshold condition for volatilization? Is it moisture alone, or soil moisture with air temperature and humidity, or atmospheric stability, or what?" Gish asks. "Before I retire, I'd like to be able to develop a model for pesticide volatilization that contains all the relevant parameters."

ARS soil scientist April Leytem and research leader David Bjorneberg use open-path ultraviolet-differential optical absorption spectrometry to determine ammonia concentrations at dairy operations in southern Idaho.
(D2243-2)

Even though the models need refining, the results have already had a payoff. "Some farmers have become more careful about how they apply herbicides to their fields, because higher volatilization levels lower efficacy and lower yields. Besides, they live where they work, and they want to protect the local environment," says Prueger. "But we still need to improve our measurements. When we find more accurate instrumentation or techniques, we can use them to reduce our margin of error in the measurement of pesticide volatilization."

At ARS's Northwest Irrigation and Soils Research Laboratory in Kimberly, Idaho, soil scientists April Leytem and Robert Dungan use photoacoustic field gas monitors to determine emissions of ammonia and greenhouse gases from agricultural operations.
(D2245-1)

Calculating the Impact of Cows

Across the country in Idaho, where the number of dairy cows has increased around 88 percent in the past 12 years, another group of scientists is collecting data on greenhouse gas emissions from dairy facilities and identifying how those emissions fluctuate daily and throughout the year. Methane, carbon dioxide, and nitrous oxide can all help trap heat in the atmosphere, and the development of particulate matter from ammonia is also a concern. (See story on "Blowing in the Wind" in this issue.)

"We've calculated some of the first on-farm emission rates for western large-scale dairies, along with emissions per cow and per unit of milk production," says ARS soil scientist April Leytem, who in 2008 was presented with the ARS Pacific West Area Early Career Research Scientist Award for her work in phosphorus cycling in the environment. "We're performing these studies on working commercial dairies, not on experimental farms."

Leytem worked on this project with several other scientists at the ARS Northwest Irrigation and Soils Research Laboratory in Kimberly, Idaho, including microbiologist Robert Dungan, agricultural engineer David Bjorneberg, and soil scientist Anita Koehn. For a year, the group monitored the emissions of ammonia, carbon dioxide, methane, and nitrous oxide from a commercial dairy in southern Idaho with 10,000 milk cows. The animals were mostly mature Holsteins that consumed a total mixed ration and produced an average of 75 pounds of milk per cow per day. The facility had 20 open-lot pens, 2 milking parlors, a hospital barn, a maternity barn, a manure solids separator, a 25-acre wastewater storage pond, and a 25-acre compost yard.

The team set out to calculate the emission rates of the four gases from three areas on the dairy facility: the open lots, the wastewater pond, and the compost yard. After they set up their instrumentation, they collected concentration data continuously for 2 to 3 days each month and recorded air temperature, barometric pressure, wind direction, and wind speed. With this data, they calculated the average daily emissions for each source area for each month.

Calves at a dairy operation in southern Idaho.
(D2244-1)

Their results indicated that, on average, the facility—animals, equipment, buildings, and all—generated 3,582 pounds of ammonia, 33,162 pounds of methane, and 410 pounds of nitrous oxide every day. This came to daily emission rates of 0.3 pounds of ammonia, 3.1 pounds of methane, and 0.04 pounds of nitrous oxide per cow—or 0.005 pounds of ammonia, 0.04 pounds of methane, and less than 0.0006 pounds of nitrous oxide for each pound of milk produced.

The team also found that the open lots were the source of the highest levels of ammonia, carbon dioxide, and nitrous oxide emissions. These areas generated 78 percent of the facility's ammonia, 80 percent of its carbon dioxide, and 57 percent of its nitrous oxide. The lots also generated 74 percent of the facility's methane emissions during the spring.

Generally, emissions of ammonia, carbon dioxide, and nitrous oxide from the open lots were lower during the late evening and early morning, and then increased throughout the day to peak late in the day. These daily fluctuations paralleled patterns in wind speed and air temperature, both of which generally increased during the day—and also with livestock activity, which picked up as the day progressed.

Emissions of ammonia, methane, and carbon dioxide from the wastewater pond and the compost were also lower in the late evening and early morning and increased during the day. Ammonia, methane, and carbon dioxide emissions from the compost peaked during June when the compost was frequently turned and when new manure was being added to the windrows. Methane emissions from the wastewater pond were lowest in April, when seasonally cooler temperatures prevailed, but peaked during October as temperatures rose.

"These studies will help producers meet air quality standards and help regulators determine what the standards should be," says Bjorneberg.

"Dairy producers have been very supportive of this work," Leytem adds. "Now we want to start improving models that state and federal regulators can use to generate estimates for on-farm emissions from commercial dairy facilities."—By **Ann Perry,** Agricultural Research Service Information Staff.

This research supports the USDA priority of responding to climate change and is part of Climate Change, Soils, and Emissions, an ARS national program (#212) described at www.nps.ars.usda.gov.

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